



Review

A review of electrolytes for lithium–sulphur batteries

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HIGHLIGHTS

- Review the current trends of research and development of Li/S electrolytes.
- Discuss how new concepts and materials contribute to solve Li/S cell problems.
- Discuss how the selection of Li-salt should be better motivated.
- Suggest/recommend approaches to better understand Li/S electrolyte functionality.

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ABSTRACT

To optimize the electrolyte is one of the most important directions to take in order to improve the Li/S battery in terms of performance – especially cell cyclability, rate capability, safety, and life-span. In this review we examine the state of the art for different choices of electrolytes; concepts, design, and materials, and how the resulting chemical and physical properties of the electrolyte affect the overall Li/S battery performance. The objective is to create an overall assessment of electrolytes in use at present and to provide a thorough basis for rational selection of future electrolytes for Li/S batteries.

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1. Introduction

The renewed interest in Li/S batteries in recent years is a response to the search for battery systems with energy densities beyond the conventional Li-ion battery. The Li/S battery chemistry can, despite being a rather modest voltage system at 2.15 V, in theory deliver a specific energy of 2567 Wh kg^{−1} and an energy density of 2800 Wh l^{−1} [1]. Today prototypes are available that can deliver 350 Wh kg^{−1}, and with promises of improvements by a factor 2 [2,3]. Thus already now, by far, the energy density of Li/S cells surpass Li-ion batteries at ca 180 Wh kg^{−1} [1] – potentially at a lower cost [4].

The reasons why we do not find the Li/S cells totally dominating the field of electrochemical energy storage, in light of the above theoretical advantages, are several practical drawbacks. The simplest observable disadvantage with a pure sulphur cathode is its

insulating nature – which is why conducting additives must be used in rather large quantities. These lower both the gravimetric and the volumetric capacity. A second drawback, and perhaps the one with most focus on, is the solubility of the long chain polysulphides (PS) formed at the cathode by reduction of the pure sulphur cathode (S₈) and/or by oxidation of short chain PS. Both phenomena reduce the Coulombic efficiency in the charging stage and the active mass viable for discharge. The parasitic reactions are also causing problems at the anode side of the Li/S cell. This is due to the fact that the species formed at the cathode diffuse through the electrolyte to the Li anode where they are electrochemically reduced and chemically reacted to insoluble Li–PS species, covering the anode [5]. A third, and a less seldom mentioned drawback, is that the lithium metal anode itself is largely metastable with respect to the electrolyte used. Thus, the SEI of a Li/S cell is related to Li–PS species. Finally, today the Li/S cells are cycled at very modest C-rates to retain the capacity. The reason is primarily limitations of mass transport both in the bulk of the electrolyte and at the electrolyte/electrode interface.

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The current Li/S development paths explored have been energized primarily by breakthroughs in the design of new cathodes. Impressive improvements have been possible in terms of addressing both i) the insulating nature of sulphur and ii) strategies and materials to retain long chain PS – much due to elegantly nano- and meso-scale tailored S/C composites. The latter problem, retaining the long chain PS, can also be seen from an electrolyte point of view. The goal being to discover how to best balance the electrolyte interplay with both PS and electrodes, why optimizing electrolyte components and compositions should also be a focus. As a side-note, there is also a scientific and cell development challenge connected with the application of new nano-sized cathode architectures. Designed to prevent PS dissolution, they do not immediately reveal detrimental electrolyte interactions.

The Li/S electrolyte development has at large been overshadowed by recent cathode development. Therefore, in recent reviews on Li/S batteries [5–7], the description of electrolytes are limited to rather broad classification of components and brief passages. However, Li/S electrolytes are a large enough subject to warrant a separate review. Furthermore, in response to the excitement over new cathode materials and the overall increase in research activities, electrolyte development has accelerated – also generating novel design concepts [8,9]. As pointed out by Zhang [5], dissolution of PS in the electrolyte is inevitable and essential for Li/S cell performance. Therefore, for long-term stability, it is needed to properly understand the influence of PS dissolution and the reactivity of PS in different electrolytes. In addition, concerns about the structural integrity of composite cathodes during cycling [9,10] and low sulphur loadings [11] have renewed the interest in Li/S liquid batteries [9,11–14]. The approach is the reverse of encapsulation, the trapping of more PS, and consists of dissolving high-order PS in the electrolyte to form a catholyte that replaces a solid cathode. The purpose of this paper is to review the types of electrolytes presently in use in Li/S batteries and also to suggest ways to rationally improve future electrolytes for future application, with enhanced performance.

The primary function of the electrolyte in a Li/S cell, as for any other electrochemical cell, is to efficiently transport ions between the electrodes (Fig. 1). This implies a high ionic conductivity, optimally targeted at achieving a Li^+ conductivity of $>10^{-4} \text{ S cm}^{-1}$ over the temperature range of operation [15]. For practical cells, high chemical and electrochemical stabilities are additional requirements on the electrolyte. A notable difference vs. the Li-ion technology is the less tough requirements in terms of the electrochemical stability window (ESW), which is “only” $\sim 2.5 \text{ V}$ vs. $\sim 4 \text{ V}$.

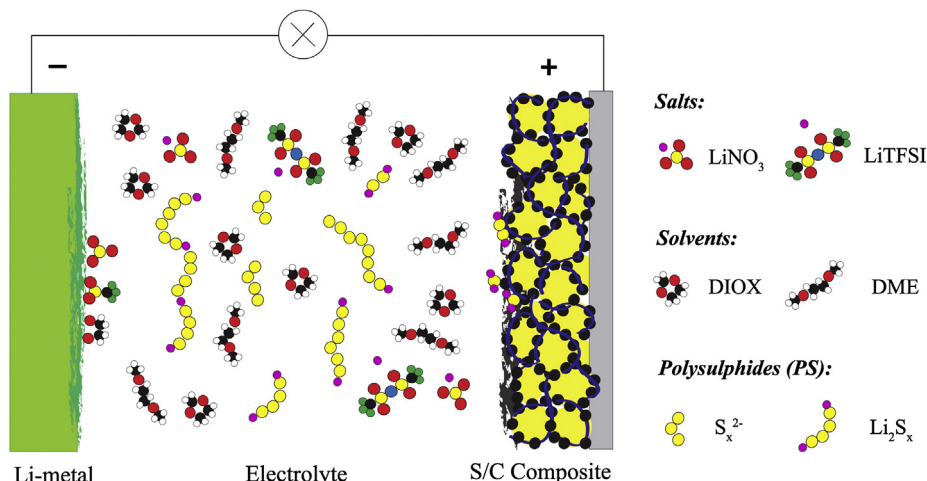


Fig. 1. Schematic of the components of a state of the art Li/S battery with an electrolyte consisting of LiTFSI and LiNO_3 in a 1:1 mixture of DME and DIOX.

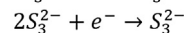
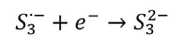
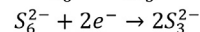
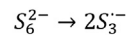
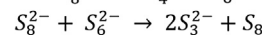
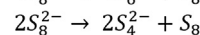
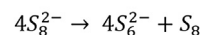
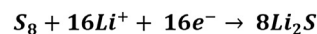


Fig. 2. The overall Li/S cell reaction (top) and examples of possible intermediate PS reactions [24,29].

This indeed opens the possibilities to use e.g. a much wider range of solvents – some of them originating from the world of primary Li-batteries. In addition to these general electrolyte requirements, the electrolyte in a conventional Li/S cell, which cannot confine most PS to the cathode, require a good solubility of the short chain PS (S_n^{2-} ; $n < 4$) i.e. the redox products of the sulphur. However, this should preferably be combined with a limited solubility of long chain PS (S_n^{2-} ; $n \geq 4$), which upon dissolution from the cathode may migrate away towards the anode. The latter is problematic due to several aspects: i) the material is now not available for further reaction at the cathode, ii) there is self-discharge taking place at the anode, iii) spontaneous deposition of solid reduction products (Li_2S_2 and Li_2S) occur, because of the poor solubility of S_2^{2-} in organic electrolytes [16,17], which increase the resistance as well as the materials loss.

All these phenomena are detrimental to both the total performance and the cyclability of the Li/S cell, albeit it should be pointed out that this “shuttling” of PS also is an inherent overcharge protection to the Li/S cell and can contribute to an improved passivation of the lithium anode surface. While the origin is quite different, the electrolyte should equally be held as mainly responsible for the limited life-length of the Li/S cells as for conventional Li-ion batteries. For the latter, degradation of the standard PF_6^- anion causes side-products, increased resistance with time, and severe safety problems [18–21]. However, for completeness, the favourable balance of properties of LiPF_6 based electrolytes should be mentioned [22]. In particular the “excellent passivation of low-potential anodes” [23] is beneficial.

A general Li-ion battery reaction scheme can be seen as modest in complexity compared to the multidimensionality

added by the intermediates during Li/S cycling. A few of the so far proposed PS reactions are presented in Fig. 2 [24,25]. This feature is in stark contrast to the deceptively simple overall Li/S cell reaction. The many possible intermediate reaction steps have been intensively researched, mainly via *ex situ* spectroscopic and spectroelectrochemical techniques [24,26–36], but also by means of direct visual observations. The $S_3^{\bullet-}$ radical ion (absorbing in the red 618 nm [27]), for example, is responsible for the blue coloration of electrolytes. Similarly, the presence and relative concentration of longer dissolved PS, such as S_8^{2-} , S_6^{2-} , and S_4^{2-} (abs. ~420–500 nm [29]), promote different yellow to red nuances of the electrolytes. Most studies of the PS distribution have combined cyclic voltammetry (CV) at inert electrodes with UV/VIS spectroscopy, but a recent exception is an *in-situ* micro-Raman study of the charge–discharge in a Li/S cell [37]. Together, these studies have found the PS distribution in Li/S electrolytes to depend strongly on the specific electrolyte composition, as well as the type of electrolyte.

By a review of the Li/S literature it is possible to identify a predominant use of non-aqueous organic liquid electrolytes, in particular binary mixtures of ethers. These systems were defined during the first years of this millennium [38]. Apart from the straight-forward route of changing the electrolyte components (salts, solvents, additives) and their relative amounts, there is also the choice of an altogether different concept e.g. ionic liquids (IL) or quasi-IL [24,39–50], or alternative high salt concentration based [8] electrolytes, solid polymer electrolytes [51–57], glassy electrolytes [58–64]. There also exist combinations of different electrolyte concepts [42,65,66]. These venues, especially the use of modern electrolyte base materials, such as ILs, have so far only been moderately explored for Li/S cells, and thus there are ample opportunities for rational improvement within a rather short time-frame.

Based on reviewing in particular the most recent scientific work the archetypical Li/S electrolyte used today is a liquid electrolyte based on a binary mixture of 1,3-dioxolane (DIOX) and 1,2-dimethoxyethane (DME) [4,14,67–81]. Usually the solvent proportion is 1:1 by volume, doped with the lithium bis(trifluoromethanesulfonyl)imide ($Li[N(SO_2CF_3)_2]$, LiTFSI) salt at ~1 M concentration. Second to this electrolyte are other liquid electrolytes based on DME or high molecular weight analogues of DME [42,44,48,53,66,75,82–99]; $CH_3[OCH_2CH_2]_nOCH_3$, $2 \leq n \leq 5$, all compounds also known as glymes (Gn); diglyme (G2), triglyme (G3), tetraglyme (G4), ...etc. In particular tetraglyme, also known as TEGDME, has been used, either as a single solvent [89,91–93,100], in mixtures with DIOX [13,38,83,95–97] or ILs [42], and also in a novel quasi-IL concept with equimolar concentration of salt and solvent [44,50].

A comprehensive summary of the various electrolyte approaches used over the years to progress the Li/S battery technology to the point where we are today is lacking. In this review the focus is on bringing together the so far scattered knowledge on Li/S battery electrolytes to form a foundation for future work based on extensive knowledge of successes and failures. In particular this is accomplished by tracing the most promising development during the most recent years.

This review is organized as follows; first the general topic of non-aqueous organic liquid electrolyte is thoroughly treated including subsections on the solvents and salts used as well as minor sections on additives and separators. Second ionic liquid based electrolytes are reviewed, both pure and mixed with organic liquids. Thereafter the review finishes with various non-liquid concepts, foremost (gel) polymer electrolytes, but also glassy electrolytes. Finally a summary is made and based on the conclusions some recommendations are provided to the reader.

2. Non-aqueous organic liquid electrolytes

The most common Li/S electrolyte concept bears much resemblance to electrolytes used for Li-ion batteries; a rather simple Li-salt with a small to medium sized anion, dissolved in a matrix of one or two solvents based on small organic molecules, often at a concentration close to 1 M. Typical electrolyte salts are lithium trifluoromethanesulfonate ($Li[SO_3CF_3]$, LiTf), LiTFSI, $LiPF_6$, and $LiClO_4$ (Fig. 3), which are combined with a variety of solvents, such as the ethers tetrahydrofuran (THF), DME, and DIOX, as well as sulphones, carbonates, and glymes (Fig. 4). Publications are also available using electrolytes based on lithium salts in IL solvents, but these are much fewer in number.

2.1. Liquid electrolytes

The convection always present, low surface tensions, and low viscosities of liquid electrolytes are all advantageous properties in order to achieve good contact between electrolyte and electrode materials. The properties enable the electrolyte to penetrate the porous cathode structure and wet the anode surface. Together with a facile transport of ions and simplicity in preparing homogeneous solutions, it is easy to appreciate the popularity of liquid electrolytes. However, the transport properties of liquids can also be a disadvantage, which for the Li/S battery is manifested in problems of dissolution and transport of intermediate reaction products and in stabilizing a lithium anode surface. The extent of these problems is sensitive to the amount and type of PS released from the cathode, i.e. depends strongly on the specific electrode configuration. Therefore, it is difficult to compare and rationalize the impact of liquid electrolytes and individual electrolyte components on the Li/S cell performance between the work of different authors. The electrode configuration and challenges for the electrolyte may be very different.

The latter point can be illustrated by the applicability of typical carbonate based Li-ion battery electrolytes in different Li/S battery configurations. Gao et al. [100], for example, demonstrated poor cell performance for carbonate based electrolytes, even when present as co-solvents in small amounts, due to the solvent reactivity towards PS species. Xin et al. [96], on the other hand, demonstrated stable performance for hundreds of cycles with an EC/DMC electrolyte in a Li/S cell using a cathode with “smaller” sulphur species. Stable Li/S cell performance using carbonate based electrolytes have been reported also with composite cathodes containing elemental sulphur [101–103]. Thus, the result is not limited to a specific cathode system, but indicates that alternatives to the more traditional PS tolerant Li/S electrolytes may be an option for specific electrode architectures. However, as noted elsewhere [5], this compatibility may be exclusive to systems with a low sulphur loading. With increased sulphur content and with a large number of charge/discharge cycles it may be more challenging to avoid PS to diffuse into the electrolyte, or worse – a collapse of the porous positive electrode [9,10].

Below we try to critically review and extract the separate roles of the three main components of liquid electrolytes: solvents, salts, and additives. Some of the chemicals used in Li/S cells originate from the field of Li-ion batteries and thus adequate and useful comparisons can be made to make use of gathered knowledge, while others are more unique.

2.1.1. Solvents

Characteristic for a liquid, as opposed to a solid, electrolyte approach is the freedom of choosing and mixing solvent components – to design an electrolyte with both specific macroscopic and molecular level properties. In Table 1 we summarize the more

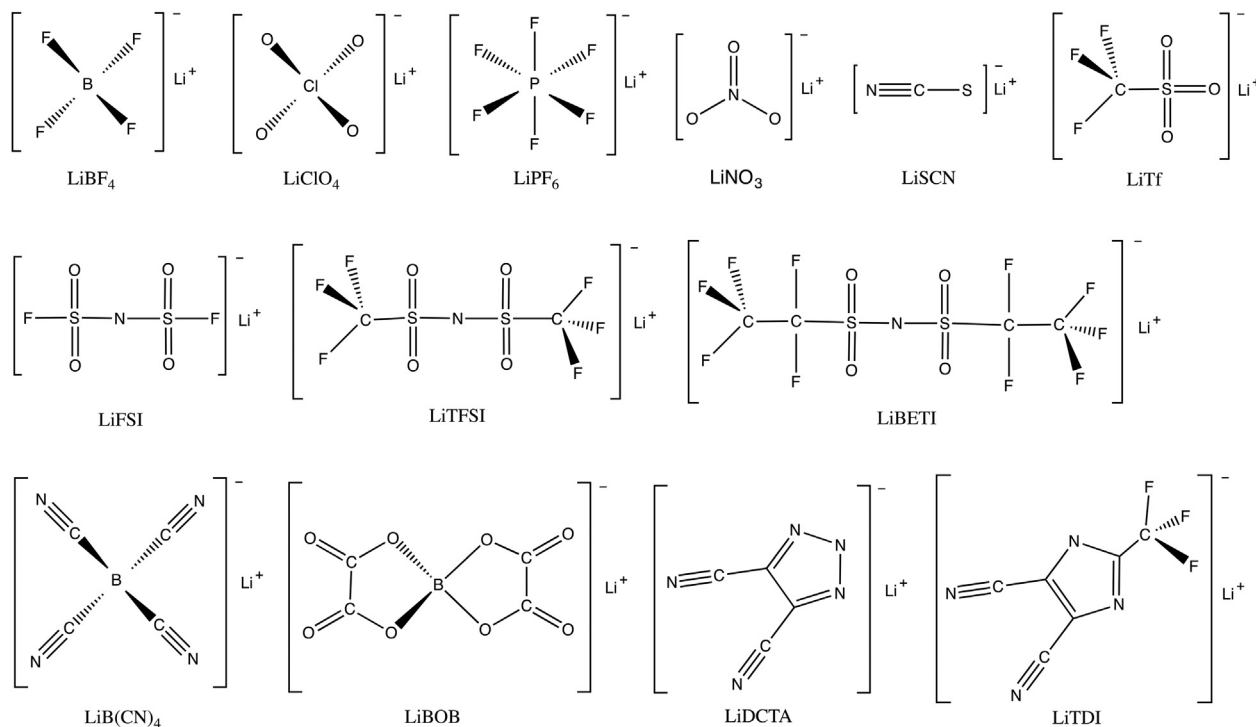


Fig. 3. Lithium salts already applied in or of potential use for Li/S battery electrolytes.

important basic physico-chemical properties for the most often used solvents (Fig. 4) [104–107]. These are both applied as single solvent matrices as well as being part of binary or ternary mixtures.

2.1.1.1. Single solvent approaches. Among the single solvents that have been applied for Li/S electrolytes, glymes of different molecular weight have dominated in the past. DME as a potential single solvent for Li/S batteries was briefly mentioned in the late 1990's [35], but since then preferentially glymes from G3 to higher

molecular weight polyethylene glycol dimethyl ethers (PEGDME), and ultimately the related solid-state matrix poly(ethylene oxide), PEO, have been used as single solvents with some success [51,84]. In recent years, with much of the PS trapped in modern S/C composite cathode materials, single-solvent electrolytes based on tetraglyme (G4) have allowed stable Li/S cell operation [92,93] and recently progressed even further with the intentional addition of a PS buffer (see Section 2.1.3) [108].

Another single solvent approach is the use of sulphones; for example ethyl-methyl sulphone (EMS), which was used together with LiPF_6 by Ji et al. [94,109]. EMS was developed as an oxidation resistant solvent for high-voltage Li-ion batteries and has a relatively high viscosity and high melting temperature, even in the presence of a lithium salt ($>0^\circ\text{C}$) [110]. Therefore, the choice of EMS as a single solvent in combination with LiPF_6 is slightly surprising. An alternative combination, EMS with LiTFSI , provides an electrolyte with both higher ionic conductivity and wider liquid range [111] and was used by Dominko et al. for an *in situ* analysis of PS species generation in a novel cell design, and compared with a corresponding electrolyte based on sulfolane (TMS) [112]. Compared to TMS, which has also both been suggested as a co-solvent in binary solvent mixtures for Li/S batteries [82] and used in a new catholyte approach (see Section 2.1.3) [9], EMS has the advantage of a lower viscosity and hence results in higher ionic conductivity electrolytes [111]. Based on a comparison of EMS based electrolytes with more traditional alternatives, Gao et al. [100] suggested EMS to be suitable for Li/S batteries only if combined with a less viscous co-solvent with a low melting point. G4, on the contrary, was suggested to be a viable single-solvent alternative [100].

Methyl isopropyl sulphone (MiPS) is a third sulphone tested for Li/S batteries [47]. It has appeared as a co-solvent for high-voltage Li-ion battery applications [113], but is less frequently encountered compared to the other sulphones. Guo et al. compared Li/S cells with LiPF_6 :MiPS and an LiTFSI :IL electrolyte [47]. Although the cells

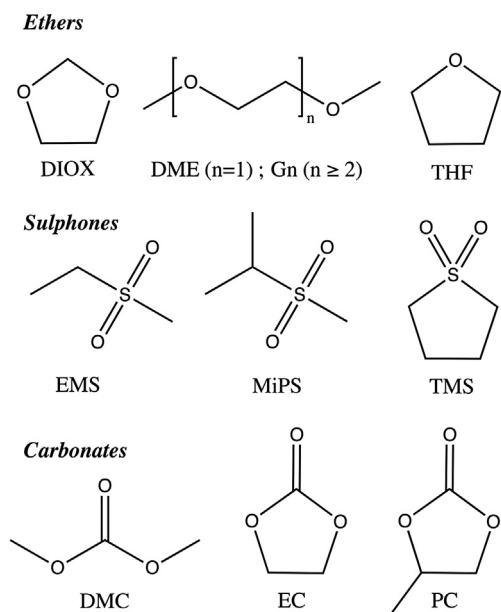


Fig. 4. Organic solvents tested for Li/S battery electrolytes.

Table 1
List of solvent basic physico-chemical properties.

Solvent	M_w (g mol ⁻¹)	T_m (°C)	η (cP)	AN	DN	ϵ
DIOX	74.08	-95	0.57	—	24	7.0
DME (G1)	90.12	-58	0.46	10.9	18.6	7.2
G2	134.18	-64	0.97	9.9	19.2	7.4
G3	178.23	-46	1.89	10.5	14.0	7.5
G4	222.28	-30	3.26	11.8	16.6	7.7
THF	72.11	-108	0.55	8.0	20.0	7.6
TMS	120.17	27	10.1	19.2	14.8	43
EMS	108.16	36	~6	—	—	95
MiPS	122.19	—	—	—	—	—

Data from Refs. [104–107].

with the MiPS electrolyte demonstrated a higher initial discharge capacity, 1080 vs. 830 mAh g⁻¹, and the best rate capability, allowing discharge at 2C, the cycling stability was inferior to the cells with the IL electrolyte. However, the comparison halted by the use of different temperatures, 25 vs. 50 °C, and choices of lithium salts, which makes it difficult to separate temperature effects, solvent, and salt contributions to the overall performance.

2.1.1.2. Solvents in binary and ternary mixtures. The many electrolyte challenges – high stability and conductivity, PS solubility *etc* – are difficult to satisfy with the use of only a single solvent. Therefore, mixtures of solvents offer a natural route forward – in analogy with their dominant use in Li-ion battery electrolytes.

The use of DIOX in liquid electrolytes has its origin in the work of Peled et al. [114], where it was introduced as a co-solvent in mixtures with either THF and/or toluene (TOL) in order to improve the conductivity. The main motivation was the low viscosity, wide liquid temperature range, and good compatibility with lithium metal. As evidenced from the electrolytes with a binary DIOX:THF (9:1 v/v) solvent mixture, DIOX has a strong beneficial effect on the ionic conductivity, ~7 times that of alternative binary mixtures explored, reaching a maximum of 7 mS cm⁻¹ at room temperature with 2 M LiClO₄ [114]. However, from the perspective of combining a high ionic conductivity with a good compatibility towards both lithium and PS, a ternary DIOX:TOL:THF (8:1:1 v/v) was found even more suitable, since TOL acts to decrease the PS solubility. A disadvantage with high DIOX concentrations was found in terms of sulphur utilization, which decreased to half when the reduction product changed to Li₂S₂ instead of Li₂S [114,115].

DME as a potential solvent for Li/S batteries was briefly mentioned in a paper in the late 1990's [35]. It has a donor number (DN) similar to THF and neither of these solvents are able to dissolve Li₂S, which affects the equilibrium between PS species. In a patent filed by PolyPlus [116], DME together with DIOX and several other neither specific donor nor acceptor type solvents were collectively categorized as suitable co-solvents for liquid Li/S cells. As a caveat, both DME and THF were recognized as potentially hazardous components for use in Li/S cells, because of their high vapour pressures and flammabilities [116], but this has not hindered their continued use, foremost DME.

Kolosnitsyn et al. suggested to use tetramethylene sulfone (TMS) with any of the ethers DIOX, DME, or THF (1:1) [82]. The Li/S cell cycling efficiency was found to strongly depend on the specific ether, explained in terms of molecular level properties; for example the depth of discharge or sulphur utilization was found to increase with decreasing molar volume of the ethers: DIOX (68.6 cm³ mol⁻¹) > THF (81.7 cm³ mol⁻¹) > DME (104.6 cm³ mol⁻¹). The maximum sulphur utilization was suggested to be caused by a higher concentration of Li-salt contact ion pairs (not measured) – increasing the electrochemical activity of the PS. Furthermore, the PS dissolved was suggested to react with

freshly deposited lithium at the metal surface. The severity of such reactions depending on both the PS concentration and the reactivity of the ether. The latter was proposed to explain the slightly worse performance of the TMS:DME based electrolyte. Overall, these differences were evident for the first few cycles, but less pronounced after >50 cycles [82].

The popular DIOX:DME solvent combination, as a function of composition and lithium salt type/concentration, was explored by Sion Power in the design of Li/S batteries for low temperature (<0 °C) operation [117]. The first discharge performance of cells at -10 °C, made using six different electrolyte compositions, suggested an optimal performance for a 0.7 M LiTf DIOX:DME (86:14 w/w) electrolyte. Increasing the DME content seems to have a strong negative effect on the performance, as seen from using LiTFSI DIOX:DME (47:53 w/w) or lithium thiocyanate (LiSCN) DIOX:DME (64:36 w/w) electrolytes [117], but neither the effect of the specific lithium salt nor the concentration was stated explicitly. The optimization of the electrolyte composition was guided by very practical considerations; achieving acceptable conductivity, lithium passivation in the presence of PS, high PS solubility and electrochemical activity.

With additional work by Sion Power on binary DIOX:DME (40:55 v/v) mixtures, a quantitative analysis of the effects of various experimental parameters on the PS shuttle mechanism was made [2,16]. No motive was given for the choice of composition in Ref. [16], where shuttle constants upon charge, discharge, and storage, were determined only as a function of salt concentration, but a summary of the benefits was presented in Ref. [2]. In particular, the low viscosity of the DIOX:DME electrolyte is crucial for good rate capability at low temperatures (<-20 °C) and readily dissolves elemental sulphur, which enables the redox reactions of sulphur to take place in solution.

Chang et al. [38] introduced solvent mixtures of DIOX and G4 as a model to understand the relation between the physical properties of the electrolyte and Li/S discharge performance. A synergistic effect on the ionic conductivity and the PS solubility was observed, with a maximum ion conductivity obtained for 1.2 M LiTf based electrolytes. The same salt concentration that gives the maximum conductivity for G4 single solvent electrolytes [38]. Dissolved PS was shown to increase the overall conductivity of the electrolyte, but pronounced changes in the PS concentration during charge/discharge also lead to large fluctuations in the ionic conductivity. Therefore, it was recommended to optimize the sulphur loading and salt concentration in combination. The behaviour of the first discharge of a Li/S cell with DIOX:G4 mixtures, in particular the length of the second plateau at 2.1 V, showed a strong dependence on the composition of the solvent mixture [38]. The best performance was obtained with a 70:30 (v/v) composition of DIOX:G4, second was DIOX, and worst was the performance of G4. The sulphur utilization, but not the ionic conductivity, was found to correlate with the trend in solvent viscosity. This result was interpreted in terms of polarization effects inside the cathode, due to PS generation, being more severe for high viscosity solvents and promoting formation of reaction products at the cathode surface. The authors did not report on the stability and performance of the electrolytes during subsequent cycles.

Revisiting mixtures of DIOX and G4, Barchasz et al. recently demonstrated optimal Li/S cell performance for 20 cycles with a DIOX:G4 ratio of 3:1 (v/v), which shows that the differences are not exclusive to the first discharge [97]. The relatively poor ability of DIOX to solvate Li⁺ and the DIOX polymerization were suggested to be responsible for a decline in performance when increasing the DIOX fraction further. Comparing 1:1 mixtures of DIOX:PEGDME ($M_{w,av}$ = 250 g mol⁻¹), DIOX:G4, and DIOX:DME in a second study they argued that the increased Li⁺ solvation ability of ethers with

extra oxygen atoms [118] improve the initial discharge capacity [119]. The initial discharge capacities of the former, 1100 mAh g^{-1} , was indeed much higher than the alternatives, 800 and 450 mAh g^{-1} , respectively, but after 10 cycles at C/10 the differences were much smaller and similar to the difference reported between DIOX:G4 electrolytes with an increase of DIOX concentration [97]. The authors did not report if also the DIOX:PEGDME electrolyte performance could be optimized by a higher DIOX content.

Some transparent research on the role of solvent composition has been presented by Samsung [120]. The discharge voltages and capacities of Li/S cells with no less than nine ternary electrolytes based on DME, DIOX, and G2 were investigated with a suggested optimal solvent composition close to DME:G2:DIOX (2:2:1 v/v). A more unambiguous comparison than usual is possible as all electrolytes were made with 1 M LiTFSI salt. Changes in the content of DME and G2 were effective in controlling PS solubility and electrolyte viscosity, and therefore the electrochemical activity of the PS. Based on cell properties measured at the 25th cycle, an equal proportion of DME and G2 was found to optimize the discharge capacity. A higher DME content increased the resistance of the cells, while a DIOX proportion of $\leq 20\%$ provided a necessary compromise of good cell cycle life and high discharge capacity, without penalizing the PS solubility and electrochemical activity too much. The conclusion was based on an analysis of both the average discharge voltage and the capacity of Li/S cells with either of the nine electrolytes.

Despite the finding that addition of G2 can improve the properties of binary DIOX:DME electrolytes, ternary electrolytes have been relatively sparsely applied and still offer room for improvements. With many electrolyte studies being more than 5 years old and in view of the development of modern composite electrode architectures, a different balance of electrolyte properties may also be required. Therefore, (re)optimization of solvent ratios and investigation of new solvent combinations will be keys to further progress. In particular, blending organic solvents with IL solvents will give a wide range of novel combinations.

2.1.2. Salts

Salts refer to the lithium salt used as the source of Li^+ for the electrolyte, with the choice guided by the chemical and electrochemical stability of the anion and how dissociative the salt is in a specific solvent. A high concentration of free Li^+ ions is always strived for, but the anion reactivity requires a balance of good film forming properties at the strongly reducing anode and resistance to oxidation at the cathode.

The most commonly used lithium salts in Li/S cells are LiTFSI and LiTf [22,121]. The reason for their popularity are mainly high thermal stability and good compatibility with ether solvents [108,122], and additionally for LiTFSI a high dissociation ability [118,123]. Furthermore, for use with an Al current collector, the lower cell voltage of Li/S batteries should not impose the same problems with Al corrosion that have plagued the use of LiTFSI and LiTf in Li-ion batteries [124]. The particularly severe corrosion in LiTf electrolytes, starting at $\sim 2.8 \text{ V}$ vs. Li [124], has for example suggested this salt to be an unlikely candidate for most other lithium battery systems [22]. Less common are LiPF_6 and LiClO_4 . The former is avoided due to generation of Lewis acids that decompose the solvents [125] and the latter for safety reasons [126].

The less stringent condition on anodic stability has renewed the interest in LiTf, but has of yet not been taken to full advantage. The choice of LiTFSI in place of LiTf in general increases the electrolyte conductivity by a factor of two [111,127] and there exist other, more recent, alternatives that should have a special potential for use in Li/S batteries. Lithium bis(fluorosulfonyl)imide ($\text{Li}[\text{N}(\text{SO}_2\text{F})_2]$, LiFSI)

[128] and lithium 4,5-dicyano-2-trifluoromethylimidazolid (LiTDI) [129] are two examples of salts of intermediate anodic stability that may provide electrolytes with conductivities that surpass those of LiTf electrolytes.

Until now there are only a few studies with focus on the role of lithium salt choice on the resulting properties of Li/S electrolytes and cells. Generally, dependencies of electrolyte properties on the choice of salt are also frequently overlooked. In a recent study by Gao et al., for example, several electrolytes based on EMS were tested with LiTf as the only salt [100], despite the much higher conductivities attainable with the use of LiTFSI [111]. On the contrary, in studies employing several lithium salts also changes in the solvent composition have been made – for one reason or the other – hinder any straightforward analysis of salt effects alone [95,96]. However, there are three notable exceptions; i) the comparison by Kim et al. using 1 M of LiPF_6 , LiTFSI, LiTf, and LiBETI (BETI = bis(pentafluoroethanesulfonyl)-imide) in DIOX/DME (1:4 v/v) electrolytes [41], ii) the work of Gao et al. comparing the properties of G4 electrolytes with 1 M of LiTf, LiPF_6 , or LiClO_4 [100], and iii) the comparison by Ueno et al. of Li/S cell performance with quasi-IL or equimolar mixtures of glyme and either of the salts LiBETI, LiTFSI, LiTf, LiNO_3 , or LiBF_4 [50].

In the work of Kim et al., noticeable differences were observed both during the initial cycles and in the rate of capacity decay during subsequent cycles. The observed differences in discharge capacity at the 50th cycle: $\text{LiTFSI} (770 \text{ mAh g}^{-1}) > \text{LiBETI} (730 \text{ mAh g}^{-1}) > \text{LiPF}_6 (620 \text{ mAh g}^{-1}) > \text{LiTf} (560 \text{ mAh g}^{-1})$ [41]. A partial explanation for the better performance of the LiTFSI and LiBETI electrolytes was inferred from the properties of these salts in PC electrolytes, with good film forming properties at a lithium surface, referring to Ref. [130]. In contrast, Gao et al. [100] concluded that the choice of lithium salt had no significant effect on Li/S cell performance of the Li/S cells tested. Yet, in Ref. [100] it is clear that the cells with LiClO_4 demonstrated a quite significant stabilization for the limited ten charge–discharge cycles made. Ueno et al. reported drastic differences in electrolyte properties and Li/S cell performance depending on Li-salt; the PS solubility was much higher in $[\text{Li}(\text{G3})]\text{NO}_3$ and $[\text{Li}(\text{G3})]\text{Tf}$ compared to the remaining electrolytes – showing a dramatic anion influence on the PS solubility [50]. A stronger interaction of Tf and NO_3^- with Li^+ and less stable $[\text{Li}(\text{G3})]^+$ complexes in these electrolytes were part of the explanation. Also the Li/S cell performance was poor with the Tf and NO_3^- containing electrolytes, as well as $[\text{Li}(\text{G3})]\text{BF}_4$, where BF_4^- was suggested to decompose in the presence of PS [50]. Thus, together with the results above, whether the lithium salt influences Li/S performance or not, seems to depend strongly on the electrolyte solvent.

Kolosnitsyn et al. compared the influence of LiClO_4 and LiTf including also the role of salt concentration on the viscosity, conductivity, and PS solubility of TMS electrolytes [131]. The viscosity increased with salt basicity, $\text{LiClO}_4 > \text{LiTf}$, possibly due to a higher concentration of free Li^+ ions available to dynamically cross-link PS chains. The Li_2S_6 PS solubility LiClO_4 concentration dependence had a minimum at $\sim 0.3 \text{ m}$, while the conductivity reached a maximum at 0.5 m . At higher LiClO_4 concentrations the electrolyte viscosity increased rapidly. While Kolosnitsyn et al. did not target LiTf concentration to study PS dissolution, Chang et al. [38] reported on this property for DIOX and G4 based electrolytes with LiTf, resulting in a recommendation of optimizing salt concentration with respect to the sulphur loading. Likewise for DIOX:G4, Barchasz et al. showed 0.1 M LiTFSI to result in low ionic conductivity, low discharge capacity, and insufficient passivation of the lithium anode. The ionic conductivity was approximately constant between 1 M and 2 M , to reach a maximum at 2 M . Overall, to balance cost and performance, 1 M was the recommended concentration.

Even higher salt concentrations than 2 M may be of interest, as experimented with Li-ion and Li/O₂ batteries [132]. Shin et al. used LiTFSI concentrations up to 5 M and monitored PS dissolution in DIOX:DME (1:1 v/v) [133]. The dissolution of PS was strongly reduced at higher concentrations and PS diffusion became slower, which significantly decreased overcharge and improved the Coulombic efficiency. In the solvent-in-salt (SIS) (≤ 7 M) electrolytes by Suo et al. [8], using an approach analogous to the polymer-in-salt concept introduced two decades ago [134], the LiTFSI salt becomes the dominant component by both weight and volume. Overall the optimal properties were found at a salt concentration of 7 M – close to the saturation limit; PS dissolution was negligible and uniform lithium metal anode plating and stripping was demonstrated. The latter was due to a high Li⁺ flux by virtue of a room temperature conductivity of $\sim 1 \text{ mS cm}^{-1}$ and a $t_{\text{Li}^+} = 0.73$, and by avoiding anion depletion at the electrode/electrolyte interface [135]. In a Li/S cell, a high initial capacity, excellent rate capability ($\leq 3\text{C}$), a high capacity retention, and a high Coulombic efficiency – close to 100% for 100 cycles were all demonstrated. A weak capacity decay was observed, but was rather attributed to an unstable S/C cathode, than to the electrolyte. As expected, the much higher viscosity (72 cP) compared to any conventional ~ 1 M electrolyte resulted in a slightly increased polarization. The most obvious drawback is cost, due to the large amount of costly lithium salt needed, for the otherwise inexpensive Li/S battery design [4]. While the SIS electrolyte concept is interesting *per se* – the generality of the promise of these very high salt concentrations beyond the use of LiTFSI remains to be verified.

2.1.3. Additives

After having covered the two main electrolyte parts, solvents and salts, the turn comes to a just as important component of a “functional electrolyte” [136] – the additives. Compared to the roles played by additives in Li-ion batteries [137], the additives used in Li/S cells are fewer in numbers, but still urgently needed. As this area is in its infancy and may rapidly change, we here provide only a small sampling to outline the major (types of) additives used in Li/S cells. The most prominent example is LiNO₃, which rather recently have been used to stabilize the Li-metal surface in DIOX containing electrolytes [138]. The functionality of LiNO₃ was investigated in detail by Aurbach et al. [139] by *ex situ* experiments on Li-foils stored in electrolytes with or without LiNO₃ – in the presence of PS. Impedance data analysis clearly showed that foils stored in electrolytes with LiNO₃ had smaller impedance than those stored without. From a qualitative surface analysis by ATR-IR and XPS spectroscopy, reduced Li_xNO_y species, together with oxidized PS, Li_xSO_y, were both suggested to form a suitable surface film passivating towards further reactions with PS. In addition also the lithium salt, LiTFSI, was suggested to have an influence on the film properties. A comparative study on short and long-term storage suggests that the film formation occurs instantaneously.

Furthermore, LiNO₃ studies by Zhang indicated that the beneficial anode passivation was accompanied by a less desired effect at the cathode [75]. During the first discharge, LiNO₃ was found to be irreversible reduced at the carbon surface, with a negative impact on the capacity and reversibility of the Li/S battery during subsequent cycles. However, by not discharging the cell further than 1.6 V, the reduction of LiNO₃ could be avoided. Zhang also recommend including LiNO₃ as a co-salt rather than as an additive, as it is indeed used in Refs. [140,141], since LiNO₃ is continuously consumed and thus eventually depleted. Usually the term “additive” is used when the amount added amounts to 5 (wt)% or less, whereafter the nomenclature “co-salt” is preferred. While also other NO_x-species provide similar passivation films [138], neither

LiNO₃ nor any alternative provides a satisfactory solution for the protection of the anode by themselves [2].

As our second example of an additive, we note that Xiong et al. suggested that a lithium surface film richer in organic components would be both more persistent and safer than films formed by the inorganic NO_x-species [78], and introduced the lithium bis(oxalato) borate (LiBOB) salt as an additive. Some beneficial effects on the initial discharge capacity and the surface morphology were observed, but with increasing cycle number, the Li/S cells without additives showed the same performance as with LiBOB added.

PS themselves can also be used as additives to improve the compatibility of the electrolyte with the lithium metal anode [9,71,108]. The liquid Li/S battery or catholyte concept [9,11–14] represents the extreme of this approach, but there are also approaches where PS are used as additives together with mesoporous S/C cathodes [108]. Cycling symmetric Li/Li and Li/S cells with 0.2 M Li₂S₆ as a co-salt in 0.8 M LiTFSI DIOX:DME (1:1 v/v), Xiong et al. demonstrated the formation of a stable two-layer interface at the lithium metal surface [71]. The top layer consisted of decomposition products of LiTFSI, due to the initial contact with the anode, and the inner lithium sulphide layer was produced from the PS additive (Fig. 5). The inner layer prevented continuous reaction of the anode with LiTFSI, but the surface film was not successful preventing the PS shuttle. However, it was suggested that the top layer could potentially be tailored to prevent the shuttle phenomenon.

With Li₂S₅ as a co-salt in 1 M LiTFSI TMS electrolytes, and the only source of sulphur, Demir-Cakan et al. investigated the performance of Li/S catholyte cells as a function of Li₂S₅ concentration and mass of Ketjen Black carbon [9]. The highest discharge capacities, 1200 mAh g⁻¹ (1st cycle) and $\sim 550 \text{ mAh g}^{-1}$ (70th cycle) at C/10, were observed at the lowest additive concentration (0.1 M), but the sulphur content (14% of total electrode mass) was too low to be practical. At higher additive concentrations (≤ 0.3 M or 54% S) the electrolyte viscosity was appreciably increased and, although quite stable over time, the resulting discharge capacities were much inferior – $\sim 500 \text{ mAh g}^{-1}$ (1st cycle) and 300 mAh g^{-1} (70th cycle) at a Li₂S₅ concentration of 0.3 M. For the first 50 cycles the cell was also inferior to a reference Li/S cell with a mesoporous S/C electrode (40% S), initially at $\sim 1300 \text{ mAh g}^{-1}$ and $\sim 200 \text{ mAh g}^{-1}$ after 70 cycles. Furthermore, analysing the surface layer of the lithium anodes from the catholyte and mesoporous S/C based Li/S cells after the first discharge, no significant differences in the surface compositions were observed. However, by way of a novel design concept for the catholyte cell – consisting of pre-forming a PS layer on the lithium anode before cell assembly – it was possible to improve both the discharge capacities and to modify the surface layer composition at the anode [9]. With a sulphur content of 34% deposited on the lithium anode, and after 10 initial conditioning cycles, the discharge capacity of the corresponding cell was for the remaining cycles 100–200 mAh g⁻¹ higher than the reference S/C based Li/S cell. The improved performance was attributed to longer PS chains and a lower Li₂S content in the anode surface layer of the novel cell.

With reference to the work above, Lee et al. reported an optimized approach using 5 wt% Li₂S₈ as an additive in LiTf:G4 (1:4 n/n), in combination with a sulphur/meso carbon micro beads (MCMB) graphite composite (1:1 w/w) as the positive electrode [108]. Interestingly, the Li₂S₈ did not affect the electrolyte conductivity, but improved the already high Li⁺ transference number from 0.8 to 0.9. In the corresponding Li/S cells, electrode dissolution was decreased by the presence of the additive, so as to preserve the initial characteristics of the positive electrode, which resulted in an impressive Li/S cell performance. Galvanostatically cycling the Li/S cells between 1.0 and 3.2 V at 35 °C, a stable discharge capacity of $\sim 1500 \text{ mAh g}^{-1}$ was maintained for 80 cycles – at both C/5 and C/3

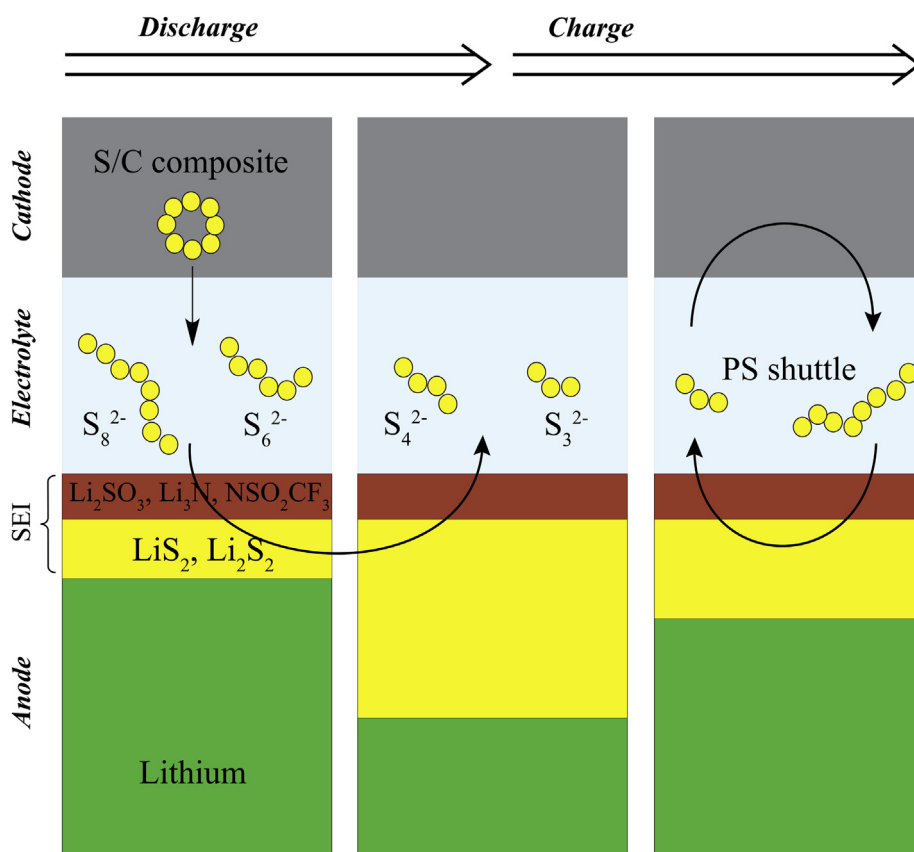


Fig. 5. Schematic illustration of electrode/electrolyte reactions in a Li/S cell with a 0.8 M LiTFSI DIOX:DME (1:1) + 0.2 M Li_2S_6 electrolyte – redrawn from Ref. [71]. Reduced polysulphides (PS) dissolve in the electrolyte to create a PS-shuttle mechanism between the electrodes that includes the formation of insoluble species at the Li/electrolyte interface.

rates [108]. Thus, PS as an electrolyte additive, at a well-defined concentration and composition, seems to be a promising route towards improved Li/S cell performance.

The above mentioned additives exemplify the main use in Li/S cells of today. For a more extensive list of additives for Li/S batteries we refer to the review by Zhang [5]. In the future the area of additives will probably prosper once the Li/S battery field has matured – this has clearly been the case for lithium ion batteries. With a similar number of phenomena needed to be addressed – and the impressive results achieved with PS as an additive – there is no reason to expect a different evolution for Li/S batteries.

2.1.4. Separators

Separators are of course not an intrinsic part of the liquid electrolytes, but are utterly needed to maintain the physical integrity of the cells. The separators used are almost always ready-made commercial alternatives originating from the Li-ion battery field. The typical choices of separator are the various polyolefins provided by Celgard [142]. These consist of 25 μm thick monolayer polypropylene (PP) with different porosity and pore sizes (Celgard 2200, 2300, 2400, 2500), surfactant coated alternatives (Celgard 3401, 3501), or trilayer PP/polyethylene/PP membranes (Celgard 2320) etc. Celgard 2400 with 41% porosity and 0.043 μm pore size is overall the most popular choice, used in $\sim 30\%$ of the studies with a Celgard type separator. Of course also alternatives to the Celgard polyolefin separators have found use; Setela [139] and Viledon [13] are two examples, and also glass fibre based separators from Advantec [44] or Whatman [96]. Despite this variety of separators available, any explicit motivation for the specific choice of separator is seldom given in the studies, not even when

including more than one separator in the same cell, such as found in Ref. [13]. Furthermore, also comparisons of different separators in the same Li/S cell design are absent, which makes it very difficult/impossible to judge the influence of the separator. However, there are occasionally small details revealed about observations having connection with the role of the separator; e.g. Gao et al. were not able to wet their trilayer separator with a single-solvent EMS electrolyte [100]. To resolve this issue, they had to prepare alternative EMS electrolytes by mixing in DEC or DIOX:DME. Indeed, the problem of sulphone based electrolytes to wet conventional polyolefin based separators has previously been described for Li-ion battery applications [143]. Dominko et al. [112] did not experience the same problem with their glass fibre based separators, neither did Ji et al. [94,109], but the latter unfortunately without any information given about the type of separator used. In agreement with the observation made by Gao et al. for liquid electrolytes [100], Shin et al. reported problems of wetting a Celgard 2400 separator with an IL (PYR14TFSI) based electrolyte, but this was resolved by creating a hybrid IL/organic electrolyte with PEGDME [144].

Overall, the influence of the separator for Li/S performance is not well documented at all – but for sure this situation is not unique to the field of Li/S cells – the role of the separator is often largely neglected. Of course this can and should be addressed through more transparent information being published about the separators used in each and every study of Li/S cells. Further progress should be possible by directed studies employing different separators in cell tests with all other parameters kept constant. For any liquid electrolyte concept it is also crucial to consider the multiple roles of the separator. In the overview of binary DIOX:DME

electrolytes presented by Sion Power [2], electrolyte consumption and the formation of a rough lithium metal surface during cycling were identified as the two main problems of Li/S batteries with liquid electrolytes. For the latter problem, separators that contain additives or act as physical barriers, protecting the lithium, are examples of actions that can and already are being pursued.

2.1.5. Summary of liquid electrolytes

Reflecting on the survey of the solvents in Table 1 and their mixtures, there is indeed a large variance in the properties of solvents implemented for Li/S electrolytes. Already in the early stages of Li/S development attempts were made to rationalize the PS solubility and reactions as a function of solvent properties, such as donicity/basicity and permittivity [29]. Deciphering the PS equilibrium in single solvents and solvent mixtures have continued, mainly by *ex* or *in situ* UV absorption spectroscopy experiments on electrolytes with Li_xS_y salts added [24,26–37]. However, as different cathode materials and designs emerge the requirements on the electrolyte will no longer be the same. They are neither uniquely defined for every system, and must thus be tailored to maximize the Li/S performance for different cell configurations. It is clear that a better understanding of the unique roles played by the solvents, lithium salts, additives, and separators is needed. Indeed, also the possible synergy of electrolyte components, would be highly beneficial to foster a future rational development and optimization of Li/S batteries. In order to accomplish this the electrolytes must be compared and studied more systematically by e.g. implementing alternative electrolytes in the same Li/S cell configuration and subsequently, in a clever way, varying the individual components – choice and material ratios. This is especially important for liquid electrolytes, with their larger degrees of freedom in composition compared to other electrolyte concepts.

2.2. Ionic liquid based electrolytes

Ionic liquids (ILs) is a class of materials that recently have attracted enormous attention for electrochemical devices in general [145], mainly due to their non-volatile and non-flammable nature. This holds promise of much safer electrolytes in terms of avoiding leakage and/or gassing and all other safety behaviour connected with thermal properties as compared to using conventional organic liquid based electrolytes. To this can be added inherent high ion conductivities, large electrochemical stability windows (ESW), and large solubility powers. The main drawbacks with ILs in electrolytes are their much higher viscosities than organic liquids used – resulting in reduced conductivities/mobility and that they at least initially are implemented at a substantially larger cost than any organic solvents used. However, at larger volumes of production or the development of organic/IL hybrid electrolytes, the resulting cell properties may nevertheless offset the remaining cost differences. In addition, the ILs themselves are so far much less studied in terms of e.g. toxicity and ageing phenomena – properties and phenomena crucial to address properly. The exact extent of importance and applicability of each of these IL properties, good or bad, of course varies from field to field, and notably relatively few publications exists where ILs have been applied as electrolyte matrices for Li/S cells. This is understandable in the light of less need for a large ESW as compared to Li-ion batteries, but all other beneficial IL properties listed above should have attracted due attention. The very first paper using ILs as the electrolyte matrix for Li/S cells appeared in 2006 [40] (being preceded by Kim et al. [39] that used ILs as additives to organic electrolytes – up to 30 vol%). Today we find close to twenty studies employing ILs in Li/S cells in some form [24,39–50,65,66,144,146].

2.2.1. Neat ionic liquid electrolytes

The main promise of ILs applied to Li/S cell is the possibility of different modes of tailoring the PS solubility properties and at the same time the overall conductivity. Indeed, often 10^{12} different possible ILs are mentioned as possible, but for electrolyte purposes we find the anions tend to be the same as the traditional Li-salt anions and the range of cations tested to be only within a rather limited range (even in terms of families of cations). Only very recently has a somewhat wider class of IL electrolytes been tested for Li/S electrolytes [146]. The physical properties determining the solubility power; charge distribution, polarity, acceptor and donor numbers, viscosity, permittivity *etc.*, are of course the same as for any other solvent, but there are two distinct differences in appearance. First, the permittivity is largely independent of the cation and anion combination used to create the IL, the variation is extremely small (and its fundamental validity still debated) – and thus likely of less importance. Second, the extreme variation in the types of cations and anions possible will affect the molecular level interactions, type and strength, possible to use for the solvation. Coulombic interactions is a main actor, but in light of the chemistries used also hydrogen bonding and even dispersion forces (vdW bonding) may play important roles. Furthermore, another very attractive aspect of using ILs as electrolyte matrices is the dominant use of the same anions as in the new lithium salts developed for battery purposes – keeping the Li-salt doped systems as simple and versatile as possible. In the literature, the TFSI anion dominates as the anion part of the ILs used as Li/S electrolyte matrices, while there is a less clear cation choice of preference. Typical examples for the latter are found in the imidazolium and pyrrolidinium families and specific examples of popular cations are the 1-butyl-3-methylimidazolium (BMIM), 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-1-methylpyrrolidinium (PYR14), and 1-butyl-1-methylpiperidinium (PiP14) cations [24,40,43,147] (Fig. 6).

In an early report Yuan et al. prepared a Li/S cell with a 1 M LiTFSI:PYR14TFSI electrolyte that provided $>800 \text{ mAh g}^{-1}$ for 10 cycles at a $\sim 0.03\text{C}$ -rate [40]. Based on the single discharge plateau at $\sim 2.1 \text{ V}$, the PS solubility was suggested to be very low in the IL, which accounted for the higher discharge capacity and improved cycling stability relative a reference cell with a 1 M LiPF₆: EC/DMC electrolyte.

In another, quite typical study, Wang et al. used EMIMTFSI doped with the corresponding LiTFSI salt in 1 M concentration and compared the Li/S cell behaviour with a cell using a 1 M LiTFSI/PEGDME electrolyte [43]. From the CV and impedance analysis, showing both better cyclability and discharge capacity, the PS were concluded to be less soluble in the IL based electrolyte. More recently, Tachikawa et al. used a so-called “quasi-IL”, [LiG4]TFSI, where the cation, [LiG4]⁺, is an equimolar complex of G4 and Li⁺, and found promising Coulombic efficiency, albeit at low C-rates (0.08) [44].

Park et al. investigated a Li/S cell with a 0.64 M LiTFSI IL electrolyte based on a quaternary ammonia cation (DEME) and TFSI [48]. The cell had an initial capacity of 800 mAh g^{-1} and maintained a reversible capacity of 576 mAh g^{-1} after 100 cycles – at 98% Coulombic efficiency. Furthermore, by a direct comparison with the same basic cell and a 1 M LiTFSI/G4 electrolyte, Park et al. showed almost unambiguously a suppressed PS solvation to be obtained using the IL based electrolyte. The remaining question mark is the role of the different salt concentrations applied. Compared to the “solvent-in-salt” SIS electrolyte concept of Suo et al. [8], the IL electrolyte of Park et al. did not lead to as efficient suppression of PS dissolution, despite the viscosity actually being higher (117 vs. 72 cP). In a very recent, and quite extensive, follow-up study Park et al. [146] even more emphasized the importance of the anion for the donor ability of the IL in the electrolyte by screening no less

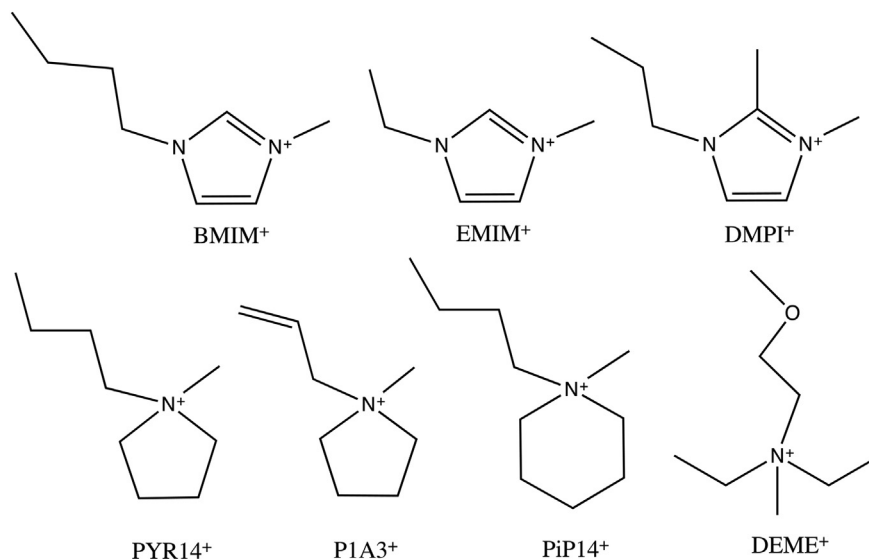


Fig. 6. Examples of IL cations implemented in Li/S battery electrolytes.

than 13 different ILs in real Li/S performance tests. The emphasis was on different FSI and TFSI ILs, but also BF_4^- , PF_6^- and Tf based ILs were studied for PS solubility and cell capacities (the latter for a salt concentration of 0.5 M and a constant current density of $139 \text{ mA g}^{-1} \text{ S}$). Notable is that no accurate PS determination for the ILs with BF_4^- was possible due to an irreversible reaction of this anion with the PS and that ILs based on Tf clearly did not suppress the PS solubility. By careful XRD studies also the FSI anion was found to decompose at the cathode in the Li/S cell tests (likely forming Li_2S and Li_2SO_4 at the surface). Thus, it is not suitable for any application – though allowing highly conductive electrolytes with low PS solubility. Overall the PYR13 cation and TFSI (weak donor anion) based ILs allowed the best sustained performance (50 cycles) in terms of capacity (up to $>650 \text{ mAh g}^{-1}$) and Coulombic efficiency (ca 98%). C-rates (for discharge) were tested up to 1C (at 60°C) allowing 500 mAh g^{-1} , which was ascribed to the 3 times higher electrolyte conductivity as compared to at 30°C (where a 1C test resulted in less than 200 mAh g^{-1}).

Yan et al. reported on additional freedom in selecting the IL cation by virtue of a less electropositive anode in place of lithium metal [46]. The Li/S cell based on an electrolyte of an allyl functionalized PYR13 (P1A3) cation in a TFSI based IL in combination with a Si/C anode and an S/C composite cathode operated at a nominal voltage of 1.5 V and delivered a capacity of 670 mAh g^{-1} at the 50th cycle (0.1C) with excellent Coulombic efficiency.

Notable overall with the use of neat IL electrolytes is the generally very low C-rates, often less than 0.1, most likely due to the high viscosities of the ILs resulting in limited ion transport. Another observation is that there are no two Li/S cells from different groups cycled in the same manner making any cross comparisons to unambiguously reveal IL electrolyte unique findings impossible. A common complicating factor is the wettability of separators with some ILs [144] (see Section 2.1.4).

Regarding PS compatibility and speciation, a recent UV–VIS spectroscopic study focused on four different ILs as electrolyte matrices; BMIMSCN, BMIMTFSI, PYR14TFSI, and PiP14TFSI [147]. CV studies using $\text{LiTFSI}_{0.1}\text{PiP14TFSI}_{0.9}$ as electrolyte showed the changes in the UV–VIS spectra, recorded *ex situ* for separators extracted from cells at different charge and discharge stages, to be connected to the PS speciation (Fig. 7). The reactions observed are primarily the very same as when using organic liquid based

electrolytes, as described in more detail by Manan et al. [24], but nevertheless a large loss of active material (precipitation) does result in a rapidly declining capacity upon cycling [147]. The latter is, however, in stark contrast to the *in situ* spectroelectrochemical observations by Li et al. [80], claiming PiP14TFSI to have low enough solubility of PS to maintain a good cyclability of the cell.

However, in none of the works cited above there is any use of molecular level descriptors for the interactions with the IL matrix to explain the phenomena observed. The lack of interpretation of the exact role of the IL matrix is predominant and only in very few cases there is any more pronounced analysis of the underlying features responsible for the specific phenomena observable. Sometimes rather odd extrapolations are made, with one typical example being choosing a larger IL cation due to a previous observation for organic liquid based electrolytes of having a slower capacity fading for solvents of higher molecular weight [40].

2.2.2. IL/organic solvent mixed electrolytes

As an alternative to neat IL base electrolytes, due to cost or property issues, the venue of IL/organic electrolytes have been explored. Already in 2005 Kim et al. prepared mixed IL/organic electrolytes by adding EMIMBETI and BMIMPF₆ to 0.5 M LiTf or

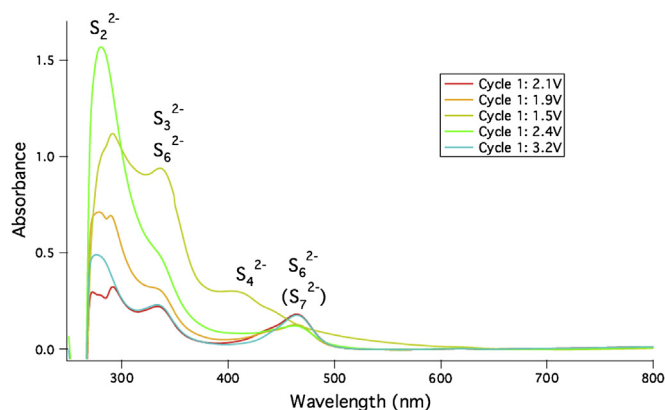


Fig. 7. The PS speciation as function of the state of charge analysed by UV–VIS spectroscopy. Reproduced with kind permission from Ref. [147]. Available in color online.

0.5 M LiPF₆ DIOX:DME (1:4 v/v), respectively [39]. Tested in Li/S cells at –20 and –10 °C, both discharge capacity and cyclability was improved by the addition of 10% IL. The difference increased when doubling the rate from 0.5 to 1C and, after 100 cycles at 0.5C, the capacity remained $\geq 600 \text{ mAh g}^{-1}$ -sulphur. Extended investigations of the LiTf based electrolyte with EMIMBETI identified a decrease in performance at an IL content above 20%. Viscosity was suggested to be more critical than ionic conductivity for the discharge capacity, because of the viscosity change being proportional to the change of the IL content. In a follow-up study, a large number of additional ILs were investigated as additives (10%) in the same DIOX:DME (1:4 v/v) organic electrolyte base [41]. By varying the imidazolium cation of the TFSI based ILs, EMIM was found to be superior to BMIM in terms of enhanced cell performance relative to using the IL-free LiTFSI DIOX:DME (1:4 v/v) reference electrolyte. Lower charge transfer resistance at the cathode surface was one of several suggested mechanisms. Interestingly, the use of a third cation, DMPI (1,2-dimethyl-3-propylimidazolium), resulted in very poor cell performance and short cycle-life. The suggested reason was an irreversible reaction of DMPI with the cathode surface.

Instead of varying the cation, the influence of the IL anion was also investigated for three IL/organic mixed electrolytes (with BMIM as the common cation and the same DIOX:DME base) with a 0.5 M LiTf concentration, identifying the imide type of anions (TFSI, BETI) to be the more suitable [41]. At the 100th cycle the discharge capacity followed the order: “BETI” (680 mAh g^{-1}) > “TFSI” (640 mAh g^{-1}) > “PF₆” (600 mAh g^{-1}). For comparison, the corresponding value for the mixed electrolyte with EMIMTFSI, in place of BMIMTFSI, as additive was 720 mAh g^{-1} . A joint analysis can be used to conclude that the cation influence is stronger than the anion influence, with a word of caution as in all of these electrolytes a 0.5 M LiTf concentration was used, implying an anion mixture in each system. Notable is also that LiTf was chosen despite earlier being found, in a comparison of IL-free electrolytes [41], to be the worst performing salt out of four.

Going to other ILs and organic solvents, here PYR14TFSI and glymes, Shin et al. investigated properties of IL/organic mixed electrolytes over a very wide composition range [42,144]. The addition of PEGDME ($M = 250 \text{ g mol}^{-1}$) to 0.5 M LiTFSI:PYR14TFSI in PEGDME:IL ratios from 1:9 to 2:1 was found to increase the ionic conductivity as a function of increased PEGDME content, but at the expense of thermal stability relative to the neat IL electrolyte [144]. Notable is that the interfacial impedance, observed for a symmetric Li/Li cell using the 1:1 ratio, was lowered compared both to the neat IL and to the neat PEGDME electrolytes, and furthermore stable for 100 days at 40 °C. The differences observed were in part manifested also in the large over-potentials measured for a neat IL electrolyte, which in Li/S tests performed very poorly. The cyclability and discharge capacity were both improved with increased PEGDME content, and the most stable performance was observed for the highest PEGDME to IL ratio [144]. Moving from PEGDME to the smaller G4 organic solvent, showed the same qualitative improvements in conductivity and Li compatibility [42], but here the Li/S cell charge/discharge was performed at very low (≤ 0.1) C-rates and with poor rate capability [42,144].

In a recent attempt to combine the benefits of organic and IL solvents Wang et al. used a 1 M LiTFSI PiP13TFSI:DME (2:1 v/v) electrolyte [66]. The motivation was a need to replace DIOX due to its propensity to react readily with contaminants, such as water and oxygen. PiP13TFSI was chosen to replace DIOX for its wide electrochemical window and high viscosity (117 cP at 25 °C) – aimed at lowering the PS diffusion rate. A Li/S cell demonstrated 50 cycles at rates $\leq 1\text{C}$, while the Coulombic efficiency was improved with C-rate and was close to 100% at 1C. The importance of the IL/organic solvent ratio was demonstrated by the overcharge being

significantly suppressed compared to a cell with an IL:DME (1:1 v/v) electrolyte [66]. Thus, in contrast to the studies mentioned above, the optimal composition was here obtained with IL in excess to the organic solvent.

As a very interesting new path of development Dokko et al. [49] pursued research on quasi-IL based electrolytes, using G3 and G4 in different ratios vs. LiTFSI (see also above). They furthermore noted a quite extraordinary power density possible for Li/S cells by adding a (non-flammable) fluorinated solvent; 1,1,2,2-tetra-fluoro-ethyl 2,2,3,3-tetra-fluoro-propyl ether (HFE). The nature of this solvent should thus also increase the safety of these electrolytes. However, from a performance point of view the important aspect is the reduced viscosity upon HFE addition and, by being a solvent of low polarity, a reduced PS solubility. The pure quasi-IL systems could reach 700 mAh g^{-1} S and Coulombic efficiencies of 98% for 400 cycles, but only with the HFE addition (ratio 1:1:4 for LiTf-SI:G4:HFE) a quite appreciable discharge capacity of ca 650 mAh g^{-1} could be obtained even at C/3 (rather than at C/10). For even higher rates, the difference between employing the two electrolytes was enhanced e.g. 510 mAh g^{-1} vs. 180 mAh g^{-1} at 1C – a most striking advance.

While there are many very interesting paths outlined above, the research on how to best balance the composition of IL/organic solvent mixed electrolytes, and which materials to base these electrolyte mixtures on, has only just begun. Guided by performance, safety, and cost there are abundant opportunities to optimize electrolytes to specific Li/S systems and applications.

2.2.3. Summary of ionic liquid based electrolytes

Based on the rather few papers above the main conclusion must be that there is ample opportunities for improvements of the concept of IL based electrolytes with respect to both the transport of lithium ions as well as to tailor the PS solvation. Of particular interest is to: i) reveal how the choice of both IL and not the least the amount of salt doping affects the electrolyte specific parts of the total Li/S cell performance, ii) test new anions when available as both Li-salts and ILs, and iii) properly assess the role of having either a pure IL or even a polymeric IL system – the latter achievable both by IL component polymerization or by mixing with other polymers (see also below).

3. Non-liquid electrolyte concepts

While liquid electrolytes “historically” and still at present dominate in the field of Li/S batteries, and IL based electrolytes have just emerged as candidates, there is a far from negligible amount of studies made using various non-liquid electrolyte concepts. The special properties of solid electrolytes e.g. solubility differences, mechanical stability, and safety increases render some of these concepts valuable as tools to study particular phenomena or to create Li/S cells with improved/changed performance. Moving from liquid electrolytes towards more solid concepts the closest step is to create *gel polymer electrolytes* (GPE). In a GPE a contained liquid electrolyte forms a gel with the polymer used – with the sole purpose to increase the mechanical performance – the main idea is to hinder PS dissolution. GPE based Li/S cells are sometimes referred to as all solid state Li/S cells – as first described in 1997 [116]. This can be motivated by the severely reduced risk for leakage, as all the liquid components conceptually are strongly contained within the GPE matrix.

As a typical example Ryu et al. [148] used a cell with a GPE based on poly(vinylidene fluoride) (PVdF) and G4 doped with LiTf, whereby two plateaus in the discharge curves could be observed, suggesting the formation of longer PS (upper plateau) and Li₂S (lower plateau). The interesting observation is that the former

disappeared after the second discharge – suggesting the GPE to hinder the dissolution of long chain PS and whereby allowing the cell a sustained discharge capacity of impressive 1028 mAh g^{-1} at $\sim C/10$ rate. GPEs have also been used for more fundamental studies; Shin et al. already in 2002 [85] studied the effect of various salts: LiTf, LiBF₄ and LiPF₆ in a PVdF-co-hexafluoropropylene (PVdF-HFP) and G4 GPE. Focus was though mixed also on the preparation technique (ball milling) to overcome the crystallinity of the polymer part, and reported discharge capacities were in the range 575–765 mAh g^{-1} (1st discharge, low C-rates). More recent and perhaps more interesting approaches are GPEs made with new types of components e.g. LiTFSI in the PYR14TFSI IL as the liquid electrolyte in a PVdF-HFP matrix [65], or a saturation with Li₂S in a system of standard Li-ion battery liquid electrolyte and a PEO framework [149].

From a more basic science perspective the ion conduction mechanism is basically expected to be very similar to what has been observed for GPEs for lithium ion batteries, being mostly liquid-like, while there is only a very rudimentary analysis of how the use of GPEs or the GPE composition in detail affects the PS solvation characteristics (which may indeed also affect the conduction mechanism to a minor extent). The blocking of PS dissolution is today mainly phenomenological and argued from a mechanical point of view.

While the PS dissolution arguably is a major problem for Li/S cells, also the meta-stability of the lithium metal anode towards any liquid electrolytes should be properly addressed. In this aspect not much is known on the performance for GPE, but making proper use of knowledge from the field of lithium ion batteries a valuable concept to stabilize the lithium metal anode surface is the *solid polymer electrolyte* (SPE). By employing an SPE a truly all solid-state configured Li/S cell with even more inherent improvements in safety based on total non-volatility and thus further reduced leakage and thermal safety risks is possible. The PS blocking properties of a GPE should, if changed in any direction, be enhanced by employing an SPE.

The SPE concept relies on the solvation power of the polymer to solvate the Li-salt and create the electrolyte and furthermore also the ion conduction is controlled by the dynamics of the polymer. This is why appreciable functionality only is found at significantly raised temperatures – often ca 70–90 °C is needed [56,125,150]. A typical SPE is based on long chain solid poly(ethylene oxide), PEO, in contrast to the related reduced chain-length, liquid analogues of PEO, such as PEGDME or even G4 [51] that have been presented as “polymer electrolytes” for use at reduced temperatures. The question remains whether the latter concepts have the same beneficial properties of totally stabilizing the lithium metal anode as a “true” SPE.

As the limited ion conductivity of the SPE hinders Li/S cell operation at faster C-rates and lower temperatures, there are approaches needed to overcome this drawback. One elegant approach is the use of nano-sized inorganic fillers, which partly can address both these issues [150–153]. The concept is sometimes named *composite polymer electrolytes* (CPE) and if the proper nanoparticles are used the balance between the charge carriers mobility is altered as visualized in Fig. 9 of ref [154]. The mechanism behind the enhanced properties has been attributed to interactions of the filler surface groups with the PEO oxygen atoms and the electrolyte anions – crosslinking polymer chains and reducing interactions with Li⁺ – to retard structural reorganizations and increase the mobility of Li⁺ [151].

The most significant break-through in using SPEs in Li/S cells in recent years was indeed made possible by the employment of nano-sized ZrO₂ as an electrolyte additive [56]. The use of SPEs with up to 10 wt% ZrO₂ was shown to enhance both the ionic

conductivity, the Li⁺ transference number, and furthermore also the electrode/electrolyte interface stability by modifying the interactions within the electrolyte, as well as forming a finely dispersed layer at the lithium surface [155,156]. However, upon addition of nano-fillers to an SPE, which almost always are semi-crystalline, the amount of crystallinity is often reduced. This can also alter the conductivity, as only the amorphous phase contributes with appreciable ion conduction. In the novel Li/S application an S/C composite cathode, a ZrO₂ and Li₂S doped LiTf-PEO CPE made possible a specific capacity of up to 900 mAh g^{-1} based on S mass and a sustained cycling efficiency of close to 100% for up to 50 cycles [56]. Though the CPE was successfully modified, it should be observed that the used C-rates were still very low (C/20), even if higher rates could be employed without irreversibly destroying the cell [56], and the temperature needed to sustain operation was still as high as 70 °C. Similar results have been presented by Liang et al. for a LiTFSI-PEO + 10 wt% SiO₂ CPE [57], where also a strong dependence on the cathode architecture was demonstrated. Although the SPE concept with or without filler has been implemented before [51–53,55], the new generation of cathode materials may provide a renaissance for SPEs or CPEs in Li/S cells.

For mainly the same reasons as employing an SPE (including CPE or a GPE) – i.e. the possibility to limit PS dissolution with the inherent safety advantages of an all solid-state cell configuration – a few groups have investigated *glassy electrolytes* for Li/S batteries [58–64]. Notable is also another advantage with glassy electrolytes – the single-ion (Li⁺) conductor nature – hence avoiding any concentration gradient and polarization problems. Hayashi et al. performed the first study on a glassy electrolyte based Li/S cell in 2003 [58], with the performance reaching 650 mAh g^{-1} for 20 cycles at room temperature with a 4:1 Li₂S:P₂S₅ glass-ceramic electrolyte. Albeit at a very low current density of 64 $\mu\text{A cm}^{-2}$. An important limitation to be aware of is that most early work using glassy electrolytes were performed with In or Cu anodes, thus alloying Li upon charging, as no functionality with a lithium anode could be sustained. In contrast, Nagao et al. [157] showed a working Li/S battery with a Li₂S:P₂S₅ + acetylene black glass-ceramic electrolyte and a lithium anode employed. Comparatively very high C-rates ($\leq 3.5C$) were obtained by pre-grinding the Li₂S added to enhance the positive electrode–electrolyte contact. Another use of glasses in Li/S cells is to create permeable protection layers on the electrodes, a crucial part of the today well-known PolyPlus technology [158].

The main limitations of all the non-liquid electrolyte concepts described above, hindering a large-scale implementation, are the inherent low conductivities at room temperature. Perhaps also the complexity of the manufacturing process compared to using liquid electrolytes, the latter either foreseen or a reality. On the advantages side, the possibility to create designed cells with controlled lower PS solubility, enhanced lithium metal anode stability, and inherently safer due to no leakage risk and thermally stable electrolytes, should be emphasized.

4. Summary and conclusions

The state-of-the-art Li/S battery electrolyte of today, $\sim 1 \text{ M LiTFSI DIOX:DME (1:1 v/v) (+LiNO}_3)$, has been gradually developed to best balance the requirements of the Li/S battery, at conditions of severe PS release. Breakthroughs in the design of Li/S materials, i.e. new S/C composite cathodes and alternatives to the lithium metal anode, have stimulated the development of a new generation of Li/S batteries and it is no longer compulsory to operate at high PS concentrations in the electrolyte. However, this development has recently been challenged by the reversed liquid Li/S concept relying on high concentrations of dissolved PS. Therefore, also the position

of the state-of-the-art Li/S electrolyte should be, and is indeed, challenged, with a wider selection of electrolytes being motivated to fully meet the new requirements of different Li/S battery concepts.

Irrespective of Li/S concept, there is room for improvement of the binary DIOX:DME solvent based electrolytes. Ternary solvent mixtures, popular for Li-ion batteries, have seldom been used in Li/S batteries, although the addition of G2 as a third solvent has been reported with improved results. Also, with the available number of ILs growing, the possibility to tailor electrolyte conductivity, viscosity, and other properties in binary or ternary mixtures is ever increasing. However, for general applicability, the use of more expensive “designer solvents” must be balanced by the extra cost – why IL/organic based electrolytes may be advantageous. The use of carbonate solvents, although dominating Li-ion electrolytes, is not a recommended alternative as in the long run the attack by PS is detrimental, the solvents are highly flammable, and are furthermore optimized for use with the moisture sensitive LiPF₆ salt – the latter to be avoided altogether.

Implementation of new lithium salts is one of the most under-represented areas of research in the field, despite the lower operating voltage of the Li/S battery that allows for a wider range of salts to be used. Frequently also conventional wisdom about the dependence of electrolyte properties on lithium salt is overlooked. The choice of LiTFSI in place of LiTf, for example, in general increases the electrolyte conductivity by a factor of two. Thus, unless motivated for other reasons, the use of LiTFSI should be preferred over LiTf. Additional room for improvement with respect to the lithium salt is the use of high salt concentrations as recently demonstrated rather drastically by the SIS concept with superior passivation of a lithium metal anode and still adequate conductivity.

Lithium salts, in particular LiNO₃, have also been the preferred additives for Li/S electrolytes, supporting the formation of a stable interface film at the Li-metal surface. However, consumed during battery operation, the required LiNO₃ concentration approach that of the main lithium salt, and is possibly still not adequate protection for long-term stability. More recently PS themselves, for long considered undesirable reaction products, have attracted attention as additives to control surface reactions and intrinsic PS release. Delicate additive cocktails, as found for Li-ion battery electrolytes, are however yet to be implemented for Li/S electrolytes. In addition, for any liquid electrolyte, the role of the separator is largely unknown, and needs to be addressed by more transparent descriptions of the separator used and by direct comparison of alternatives.

Overall, to be able to rationally improve the electrolytes for Li/S batteries, the focus must be on final Li/S cell total performance. A proper scientific identification of the processes where the electrolyte properties and performance are limiting factors is crucial. From the collected data above such analysis is unfortunately not to be found to any large extent. The electrolyte analysis is often either based on *in situ* observations for an entire Li/S cell (or at best for a set of specific electrode/electrolyte combinations), or in those cases where the unique role of the electrolyte can be extracted – it is often in model experiments using *ex situ* techniques. Proper *in situ* analysis and special cells are needed for a more fundamental understanding. This can either be general or specific to certain electrolyte concepts. Based on the survey presented herein we conclude this review with a list of recommendations for future Li/S electrolyte research.

5. Recommendations

- The knowledge on Li/S electrolytes is to a large extent either phenomenological based on Li/S cell data or when traceable to

specific physical properties, obtained *ex situ*. More emphasis on systematic studies using both *in situ* and *ex situ* approaches with the same basic cells and/or electrolytes would provide a more solid base for rational improvements.

- When possible the knowledge gained within the Li-ion battery field e.g. the role of the choice of Li-salt for the overall conductivity, should be used to rationalize the development. There is no need to address “older” materials unless it can be uniquely motivated.
- The safety issues must be emphasized in the choice of materials and in the cell design – which may give IL based electrolytes or IL/organic concepts special advantages. Nevertheless, the overall functionality of the Li/S cell and the cost issues must also be kept in focus.
- Extensive *in situ* and/or *ex situ* studies of the role of Li-salt concentration/ionic strength for the PS solvation, especially when using ionic liquid matrices are urgently needed. There are so far only limited studies where the role of this parameter is mapped in a convincing manner.
- For any rational development the detailed molecular level interactions responsible for both limiting the PS solvation and stabilizing the electrode/electrolyte interfaces must be addressed properly. New models should be developed as there is basically no precedence to be found in the literature. Typical electrolyte and component physical properties to be addressed are: polarity, DN, AN, coordination, *etc.*
- Any use of “other electrolyte concepts” should be judged from case-by-case – but to be used only sparsely – it may be needed to unambiguously reveal a specific mechanism or allow a special experiment. However, it should not be an electrolyte of choice for the final design – as the review does not convey any prospects of major advances for a simple ambient temperature Li/S cell.
- The exact role of the separator at the molecular level is largely unknown, but pending on cell design there are macroscopic effects traceable to the choice made. It would be wise to cover a few different separator choices in order to not limit the Li/S performance by this cell component. Typical separator parameters to examine/map are wettability, porosity, and electrolyte retention.

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